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Thermal and Mechanical Properties of Zeolite Filled Ethylene Vinyl Acetate Composites

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Abstract

Ethylene vinyl acetate (EVA) composites filled with zeolite (25 vol.%) were prepared using an internal mixer followed by compression molding machine. In order to enhance the thermal properties and fire retardancy of the composites, an intumescent flame retardant consisting of ammonium polyphosphate (APP)/pentaerythritol (PER) was incorporated into the composites. Two kinds of flame retardants were used which are untreated APP (APP1) and silane treated APP (APP2), where their effectiveness was evaluated by means of differential scanning calorimetry (DSC) and also thermogravimetric analysis (TGA). The results showed that both types of flame retardants have the ability to enhance the thermal stability of EVA/zeolite composites by producing charred layer which protects the underlying composites from the action of flame. Moreover, the incorporation of APP1 and APP2 has a significant effect on the composites degree of crystallinity. Meanwhile the results of tensile testing showed that the composites with APP2/PER exhibit better tensile properties compared to that with APP1/PER. This is expected since the application of silane-treated APP (APP2) could improve the dispersion of APP particles within EVA matrix.

Keywords: EVA; zeolite; intumescent flame retardant; thermal stability; flammability.

1. Introduction

The application of renewable resources filler in polymer composites has attracted the attention of many researchers due to their many significant advantages over synthetic fillers. Recently, numerous types of natural resources are incorporated in polymers including rice husk, kenaf, wood and also sugar cane [1]. However, the investigation on zeolite as natural filler in polymer composites is still limited and much work needs to be done related to its application. The use of natural zeolite as filler provides many

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beneficial properties because of its environmentally friendly characteristic, accessibility, relative cheapness and unique features for instances porosity, crystal structure and composition. Generally, zeolite is a spectrum of inorganic materials known in diverse applications such as molecular sieves, catalysis, and ion exchange materials due to their regular pore structure [2,3]. But they are also known as mineral fillers in polymer matrices. Crystalline zeolite is a framework of alumino-silicates based on infinitely extending three-dimensional networks of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of all oxygens [4]. Zeolite also has highly variable amounts of H_2O in generally large voids of the framework [5]. Ethylene-vinyl acetate (EVA) is a commonly used thermoplastic both in academic and industry area. In this research, EVA is chosen as matrix as it contains a polar group (vinyl acetate) which can effectively interact with inorganic filler such as zeolite meanwhile its fully saturated backbone provides excellent resistance towards heat, ozone and weather [6]. In addition, EVA has been marketed for wire and cable industry as a substitute of polyvinyl chloride due to its halogen-free chemical structure.

The application of zeolite filled polymer composites including EVA/zeolite composites in wire and cable industry is limited because of poor thermal stability and fire behavior of the constituents. The flame retardant behavior of polymer composites can be fulfilled by using flame retardants like alumina trihydrate, magnesium hydroxide or intumescent systems based on nitrogen or phosphorous based composunds in order to prevent the burning of the composites [7].

Although many studies [8,9] are related on improving the flame retardancy of polymer composites via adding variation of flame retardants as mentioned earlier, not much attention seems to have been paid on EVA/zeolite composites particularly using intumescent flame retardant (IFR) system. In this study, IFR system consisting of acidic source and blowing agent which is ammonium polyphosphate (APP) with the char-forming agent, pentaerythritol (PER) are incorporated into EVA/zeolite composites. It is generally accepted that IFR additives are significantly more effective than halogen-containing flame retardants. This is because those halogen-containing flame retardants have been known to impart smoke, toxic gas and also acidic fumes which obviously can harm people and environment [10].

Despite the enhanced flame retardancy of EVA/zeolite composites, the incorporation of the IFR additives significantly leads to deterioration in the composites mechanical performance. This problem arises from weak interfacial bonding between the hydrophilic zeolite and hydrophobic EVA itself, and also between the flame retardant particles and EVA matrix. Previous work has shown that the mechanical properties of composites can be attained by using compatibilizer or coupling agent [11]. For this reason, silane-treated APP particles (APP2) are incorporated into EVA/zeolite composites in order to improve the interfacial adhesion between the constituents.

Therefore, the main objective of this study was to investigate the effect of IFR consisting of APP and PER on the properties of EVA/zeolite composites. Besides, the influence of silane-treated APP particles (APP2) in improving the mechanical performance of the composites system was also investigated. The thermal properties of EVA/zeolite composites were measured with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Meanwhile, the influence of silane treatment on the composites system was determined by means of tensile testing.

2. Experiment

The compounding process was done by using Thermo Haake Polydrive with Rheomix, internal mixer. The compounding condition was set at 130 °C for 7 min. For EVA/zeolite composites containing flame retardants, the mixing time was extended to 15 min in order to obtain good dispersions of APP and PER particles within the EVA/zeolite composites. Next, moulding was done using a compression moulding machine, Gotech GT-7014-A30C, Taiwan model. The process was performed at temperature of 130 °C. The compound was pre-heated for 8 to 12 min followed by compression for 2 min at pressure of

approximately 10 MPa. After that, the compound was transferred into cooling platen and allowed to cool down for 4 min under the same pressure which is 10 MPa.

The tensile properties were determined using electromechanical Instron machine, 3366 model. The tensile test was conducted according to ASTM D 638 with specimen dimensions of 150 mm × 120 mm × 1 mm. The cross head speed was 50 mm/min meanwhile the gauge length was 50 mm. The mechanical properties such as tensile strength, elongation at break and Young modulus were determined by calculating the average values of the five tested dumbbell-shaped samples.

The thermal study was carried out on a PerkinElmer Pyris TGA-6 thermogravimetric analyzer in order to determine the weight losses and thermal decomposition temperature of the EVA/zeolite composites. Sample was weighed to approximately 10-15 mg. The analysis was done at a constant heating rate of 20 °C/min and under a flow of pure nitrogen at 20 mL/min. The temperature ranged from 20 to 600 °C.

DSC analysis was carried out with a Perkin Elmer Pyris DSC-6 instrument under flowing nitrogen atmosphere. Samples of EVA/zeolite composites were weighed to approximately 15 mg and placed in an aluminum pan. Samples were then heated from 30 to 190 °C at a rate of 10 °C/min and held at 190 °C for 2 min in order to eliminate the previous thermal history (first heating run), then they were cooled to 30 °C at 10 °C/min and reheated under the same conditions to 190 °C (second heating run). Phase transition temperatures and enthalpies were recorded for each sample, respectively, from the maxima and areas of the crystallization and second run melting peaks. The crystallinity degree for the composites is determined by the ratio ΔH_m / ΔH_{m100}, where ΔHm is the heat of fusion in joule per gram polyethylene segments in the EVA samples meanwhile ΔH_{m100} is the heat of fusion in joule per gram pure polyethylene with 100% crystallinity. The ΔH_{m100} is 281 joule per gram pure polyethylene with 100% crystallinity.

3. Results and Discussion

Figures 1-2 show the tensile properties of EVA composites at 25 vol.% of zeolite loading. It can be seen that EVA/zeolite composites exhibit the highest tensile strength and elongation at break, but the lowest tensile modulus in comparison with the EVA composites in the presence of IFR (APP and PER). The incorporation of both APP and PER particles into EVA/zeolite composites results in the reduction of the composites tensile strength and elongation at break. However, the tensile modulus or stiffness of EVA/zeolite composites was significantly increased with the addition of the IFR particles. The deterioration of the tensile strength and also elongation at break for EVA/zeolite/IFR composites could be attributed to incompatibility and weak adhesion between the IFR and EVA matrix. This is in perfect agreement with the results reported by Demir *et al.* [12]. Apparently, EVA/zeolite composites with APP2/PER exhibit better tensile properties compared to the composites with APP1/PER. The increment in tensile properties is believed due to the application of silane-treated APP, which is APP2 that could improve the dispersion of APP particles within EVA matrix. However, the application of AMPTES-treated zeolite into the composites did not significantly improve the tensile properties of EVA/zeolite/IFR composites.

Table 1. TGA results of EVA matrix and its composites

Composites system	T_5 (°C)	T_{90} (°C)	T_{100} (°C)	Char residue at 600 °C (%)
25% EVA/zeolite	35.06	397.04	440.85	37.33
25% EVA/zeolite/APP1/PER	40.09	448.61	497.71	43.64
25% EVA/zeolite/APP2/PER	40.16	454.78	504.65	45.24
25% EVA/zeolite/AMPTES/APP2/PER	42.09	465.17	506.93	46.74

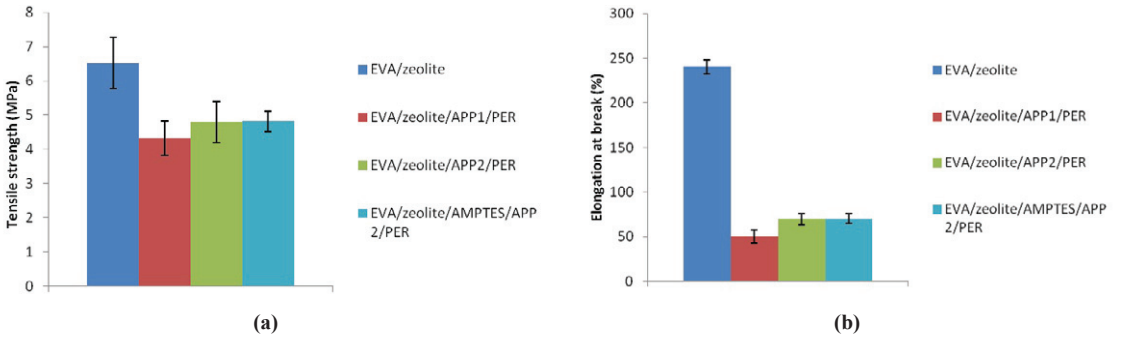


Fig. 1. (a) Tensile strength and (b) elongation at break of EVA composites at 25 vol. % of zeolite content

TGA curves of composites with IFR system (APP and PER) exhibits different thermal behavior compared to that of without IFR, as presented in Figure 3. By referring to the DTG curves of composites with IFR, a peak between 280 °C and 350 °C was attributed to the development of intumescence and the intumescence coating degrades between 350 °C and 430 °C. At higher temperatures, there are structural changes leading to formation of new carbonaceous species up to 490 °C [12]. It is clear that the incorporation of APP and PER into EVA/zeolite composites had significantly increased the thermal stability of the composites for instances, the maximum degradation temperature of the composites shifted from 440.85 °C to 497.71 °C and 504.65 °C for EVA/zeolite/APP1/PER and EVA/zeolite/APP2/PER composites, respectively. Furthermore, the presence of APP and PER also increased the char residue of the composites at 600 °C, as summarized in Table 1. The improvement in thermal stability of EVA/ zeolite/APP/PER composites could be caused by the good thermal stability of the carbonaceous material or char formed during the decomposition process of the composites. The char residue is one of the most important parameters used for comparing thermal stability. This is due to the formed char layer has the ability to protect the underlying composites from decomposing and hence prolongs the thermal decomposition temperature of the composites [13]. During the combustion, the reactions between APP (acid source and blowing agent) and PER (charring agent) cause the expansion of char which consequently developed a large volume of high carbon protective layer that effectively protects the underlying EVA/zeolite composites from the attack of heat or flame.

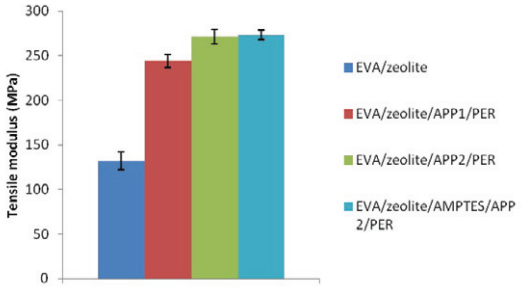
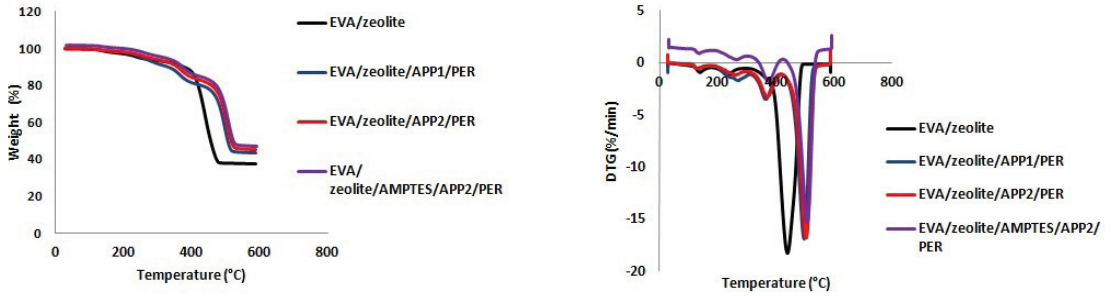


Fig. 2. Tensile modulus of EVA composites at 25 vol. % of zeolite content

As listed in Table 1, EVA/zeolite/APP2/PER exhibits higher thermal stability in terms of all T_5, T_{90} and T_{100} than that of EVA/zeolite/APP1/PER composites. This is might be due to improved compatibility between silane-treated APP particles (APP2) and EVA matrix. The thermal stability of silane-treated

zeolite filled IFR composites was also higher than that of unmodified ones, probably because of the better dispersion of silane-treated zeolite within the EVA matrix. As compared with that of unmodified IFR composites, the char residues after degradation of silane-modified IFR composites at 600 °C is slightly higher which indicates the enhancement of their flame retardancy with the application of surface treatment.



(a) (b)

Fig. 3. (a) TGA thermograms and (B) DTG curves of EVA and its composites having 25 vol. % of zeolite loading

Figure 4 shows the heating melt DSC curves of EVA/zeolite composites and IFR-containing EVA/zeolite composites. The melting temperature and degree of crystallinity of the composites are also outlined in Table 2. It is apparent that the incorporation of PER with APP1 and APP2 into the EVA/zeolite composites had significantly increased the melting temperature of the composites from 89.07 °C to 91.07 °C and 91.63 °C, respectively. It can be inferred that the IFR (APP/PER) has the ability to reinforce the thermal stability of EVA/zeolite composites with their heat resistance [14]. As compared to the EVA/zeolite/APP1 composites, the melting temperature of EVA/zeolite/APP2 composites is slightly higher. Obviously, the higher melting temperature could be ascribed that better dispersion of APP2 fully embedded on EVA matrix.

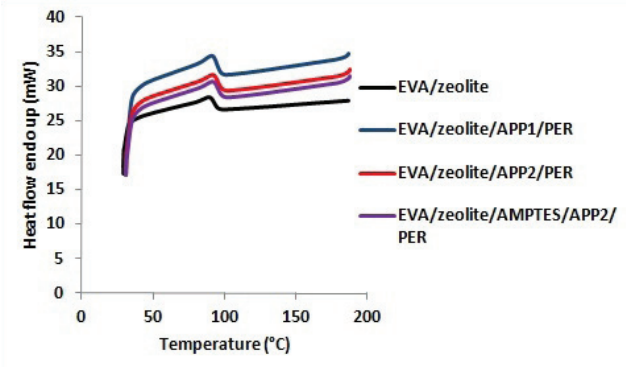


Fig. 4. The heating melt DSC curves of studied composites having 25 vol. % of zeolite loading

For the composites with IFR system, it is found that EVA/zeolite/APP2/PER composites possess lower crystallinity degree compared to that of EVA/zeolite/APP1/PER composites. This is possibly due to the APP2 particles in the composites was initially treated with silane coupling agent hence exhibits improved compatibility with the EVA matrix. The improved APP-EVA matrix interfacial adhesion results in greater

effect in imparting physical hindrance to restrict the molecular chains mobility of EVA. Consequently, the EVA chains become less flexible thus making the crystallization more difficult.

Table 2. DSC results of EVA matrix and its composites

Composites system	Melting temperature (°C)	Enthalpy of fusion(J/g)	Degree of crystallinity (%)
25% EVA/zeolite	89.07	19.65	6.99
25% EVA/zeolite/APP1/PER	91.07	6.69	2.38
25% EVA/zeolite/APP2/PER	91.63	6.12	2.18
25% EVA/zeolite/AMPTES/APP2/PER	91.70	6.09	2.17

4. Conclusion

Incorporation of IFR particles (APP and PER) increased the stiffness but decreased the strength and ductility of EVA/zeolite composites. However, EVA/zeolite/APP2/PER composites show higher value of tensile strength, elongation at break and tensile modulus than those of EVA/zeolite/APP1/PER composites. This might be attributed to the improved compatibility between EVA composites and silane treated APP (APP2). TGA and DSC results indicate that the thermal properties of EVA/zeolite composites containing IFR exhibit higher melting and thermal decomposition temperature compared to that without IFR.

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